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 Entwurfs- und Herstellungsverfahren einer mit festen ionenleitenden Elektrolyt versehene Anordnung

 Procédé de conception et de fabrication d'un dispositif à électrolyte solide conducteur d'ions
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- (56) References cited.

WO-A-87/02593 US-A- 4 279 974 DE-A- 1 809 878 US-A- 4 413 041

- PATENT ABSTRACTS OF JAPAN vol. 16, no. 048 (E-1163)6 February 1992 & JP-A-03252059
- PATENT ABSTRACTS OF JAPAN vol. 13, no. 374 (E-808)(3722) 18 August 1989 & JP-A-01128361
- PATENT ABSTRACTS OF JAPAN vol. 15, no. 229 (E-107)11 June 1991 & JP-A-93067468
- PATENT ABSTRACTS OF JAPAN vol. 14, no. 55 (E-882)(3998) 31 January 1990 & JP-A-01279576

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Description

The present invention relates to ion conducting devices, and more particularly to current based ion conducting devices arranged into a stack of electrically interconnected solid electrolyte plates.

Ion conducting devices based on solid electrolytes are typically constructed according to two basic designs. Passive ion conducting devices detect the electromotive force potential across the solid electrolyte due to the Nemst voltage generated when different ion concentrations exist on opposite sides of a membrane. Passive devices are used in a variety of applications including automotive sensors and process gas analysers. Current based ion conducting devices depend on the transport of ions through the electrolyte due either to a pressure differential across the electrolyte, or from an applied electromotive force. Current based devices are more complex in construction and operation, but have wider range of applications Well known applications for current based devices include fuel cells, inert gas purifiers, oxygen concentrators, and steam electrolysers.

An electrode material is attached to the electrolyte surfaces, the composition of which depends on the intended application and operating conditions. Reactant gases contacting the electrode undergo a reaction whereby an ion species is generated which migrates through the electrolyte. For example, in an oxygen concentrator the ion species is O-2, and is formed according to the following reaction:

$$O_2$$
 (from air) + 4e $\rightarrow 20^{-2}$

The O⁻² migrates through the electrolyte due to an applied electromotive force. Pure oxygen may be collected on the opposite side of the electrolyte according to the following reaction:

$$20^{-2} \rightarrow 20_2 + 40^{-1}$$

In a fuel cell, an electrical potential is produced between a cathode and an anode which are in contact with different concentrations of ions. When the electrodes are connected in an electrical circuit, the electrons released at the anode fumish an electrical current

Several US patents teach solid oxide electrolytes arranged in various structural configurations. US-A-4,664,987 teaches a fuel cell arrangement using a tubular configuration for the solid oxide electrolyte. US-A-4,950,562 teaches a flat plate solid oxide electrolyte configuration. Several US Patents teach fuel cell assemblies comprising a stack of solid oxide electrolyte elements. These include US Patent Nos. 5,069,987, 5,049,459; 5,034,288; and 4,950,562. In each of these arrangements, successive electrolyte elements are separated from the elements above and below by an

inert interconnector plate, or separator. The interconnector plates prevent reactants and products from mixing, yet permit the reactants to come in contact with the electrode surfaces. US-A-4,877,506 teaches an oxygen pump employing a stack of solid oxide electrolyte elements, and using inert interconnector plates between successive elements.

The interconnectors in these current based devices are part of an electrical circuit and must either be constructed from an electrically conductive material or must include an electrical pathway. Electrically conductive materials suitable for incorporation into a flat plate ion conducting device are less expensive than the electrolyte material. The interconnectors may be constructed from the expansive electrolyte material, in which case the electrical pathway is either incorporated into the interconnector, or attached to the exterior. If the solid electrolyte is used, extremely expensive material is used for inert plates which comprise approximately 50% of the stack. On the other hand, if electrically conductive material used, dissimilar materials are incorporated into the stack.

Several problems inherent in these stacked arrangements make them unreliable, inefficient, and expensive. A typical operating temperature range for solid oxide ion conducting devices is 800-1000°C. Substantial thermal expansion of materials occurs when materials are heated to these high temperatures. The different rate and extent of thermal expansion between dissimilar materials can cause cracks and distortions in the stack. Leaks may develop between the electrolyte and interconnectors, allowing reactant gases to escape before contacting the electrode. Product gases may also escape through cracks in seams or materials. These factors severely reduce the efficiency and reliability of the device. If delamination between stack components is severe enough, total failure of the device may result.

Another disadvantage of using dissimilar materials is the difficulty in maintaining an intact electrical interconnect system. Problems with contact resistance frequently result when the interconnectors are bonded to different materials. The different coefficients of thermal expansion tend to crack and destroy the conductive material. These problems are obviously undesirable in space applications, where the device must remain reliable for an extended period of time, while exposed to extreme thermal and vibration stresses.

Interconnectors also significantly reduce the efficiency of a stack of electrolyte elements. Because the plates are inert, approximately 50% of the components of the stack are inactive. The interconnectors also must seal against the electrolyte plates. Wherever the interconnector contacts the electrode, gas transport through the electrode to the electrolyte surface tends to be limited. The reactive electrolyte area available for ion conduction is thus potentially reduced through the use of inert interconnectors

Interconnectors made from electrolyte material

contribute significantly to the cost of an ion conducting device. The material itself is very expensive, and approximately one interconnector is required for every active electrolyte plate. Complex manufacturing methods are required to produce an interconnector with a typical dual ribbed structure. These factors make manufacture of ion conducting devices with interconnectors more difficult and complicated, which increases both cost and manufacturing time.

It is an objection of the present invention to provide a solid oxide electrolyte ion conducting device which overcomes the aforementioned problems.

According to the invention, there is provided an electrochemical device comprising a plurality of solid ion conducting electrolyte and plates a plurality of spacers disposed between successive electrolyte plates with an individual spacer spacing adjacent electrolyte plates apart, the electrolyte plates and spacer forming a monolithic stack, and in which, the electrolyte plates each have a pair of generally flat opposed surfaces with electrode material adherent to a significant portion of each flat surface; the spaces between a plurality of successive pairs of spaced apart adjacent electrolyte plates detining a plurality of chambers, the electrode material on the flat electrolyte surfaces being electrically connected in series whereby the electrodes on alternate electrolyte plates are electrically connected in series from one end of the stack to the other in a first electrical path, and the other alternate electrodes not connected in the first path are electrically connected in series in a second electrical 30 path, the first and second path being connected together, the first and second paths and electrodes connected thereto thus forming a complete electrical circuit; characterised in that the spacers include a plurality of first spacers and plurality of second spacers, the first and second spacers alternating to separate successive electrolyte plates, each first spacer consisting of a pair of bars and each second spacer consisting of a Ushaped bar or multiple pieces configured and arranged to form a U-shaped bar, the electrolyte plates (14) have at least one square corner (16) and at least one chamfered comer (18) the means for electrically connecting in series the electrode material on the electrolyte plates comprises at least one stripe of electrically conductive material adherent to each of the first and second surfaces, the stripe extending from the electrode material to the edge of the square comer thereby providing an electrical pathway between the electrode material and the square corner; and the electrode material further comprises electrically conductive material adherent to the chamfered corners of the electrolyte plates and the spacers which thus form a plurality of electrical pathways

According to another aspect of the invention, there is provided a method of assembling and electrically connecting a plurality of solid oxide electrolyte plates into a monolithic electrochemical ion conducting device characterised by the steps of applying electrode material to

a substantial portion of each of the two opposed surfaces of each of the electrolyte plates heating the electroded electrolyte plates to a temperature sufficient to bond the electrode material to the electrolyte plates; applying an electrical interconnect material to the electrolyte plates to from an electrical pathway between the electrode materials and the exterior of the device, applying sealing material to a portion of the electrolyte plates: stacking a plurality of the electrolyte plates in a pattern in which each plate is separated from adjacent plates by a solid oxide spacer; thermally treating a stack of the electrolyte plates and spacers at a temperature sufficient to activate the sealing material to seal the spacers and the electrolyte plate into a monolithic unit; electrically connecting in series every afternate electrolyte plate in the stack by connecting the electrical interconnects of every alternate plate from one end of the stack to the other in a first electrical path, extending the electrical pathway around the end of the stack, and connecting the electrical interconnects of every other alternate plate in a second electrical pathway, the first and second electrical pathways and electrodes connected hereto forming a complete electrical circuit; and in which the spacers include a plurality of first spacers and plurality of second spacers, the first and second spacers alternating to separate successive electrolyte plates, each first spacer consisting of a pair of bars and each second spacer consisting of a U-shaped bar or multiple pieces configured and arranged to form a U-shaped bar the electrolyte plates (14) have at least one square comer (16) and at least one chamfered corner (18) the means for electrically connecting in series the electrode material on the electrolyte plates comprises at least one stripe of electrically conductive material adherent to each of the first and second surfaces, the stripe extending from the electrode material to the edge of the square corner thereby providing an electrical pathway between the electrode material and the square corner; and the electrode material further comprises electrically conductive material adherent to the chamfered corners of the electrolyte plates and the spacers which thus form a plurality of electrical pathways

The ion conducting device and manufacturing method of the present application are useful for a variety of current based devices including fuel cells, oxygen concentrators, inert gas purifiers, and steam electrolys-

The invention provides an improved, yet simplified design and manufacturing method for a flat plate ion conducting device. The design and method obviate many of the disadvantages inherent in existing designs. The design provides an arrangement which is lighter and more compact, yet provides increased ion conducting capacity. Spacer elements are used in place of interconnectors, and are preferably manufactured from the same material as the electrolyte plates. The expensive electrolyte material may be used because the spacers can be much smaller than interconnectors. The

weight of the device is also reduced as a consequence of these improvements. Preferably, all structural components of the device are constructed from the same material and so cracks and distortions from thermal expansion of dissimilar materials are substantially eliminated.

The improved design uses a flat plate configuration for the solid ion conducting electrolyte elements. Each element has a gas permeable electrode material attached to at least one surface. Typical electrolyte/electrode systems for use in the invention of the present application are disclosed in US Patent Nos. 4,725,346, 4.879.016 and 5,021,137. The type of electrode material may depend on the intended application and operating conditions. According to the manufacturing method, electrode material may be screenprinted onto the electrolyte plates in the desired pattern. Similarly, other electrically conductive materials, such as electrical interconnections between the electrolyte plates and current collector grids, may be screenprinted onto the electrolyte plate as required.

The plates are stacked in an arrangement whereby each plate is separated from adjacent plates preferably by ceramic spacers. In a preferred arrangement, each plate in the stack has two adjacent square corners and two adjacent chamfered corners. All corners of the spacers are preferably chamfered. An electrically conductive material may be applied to the surface of the plates as two stripes connecting the electrode material to the edge of the square corners. Two-piece spacers allowing through-flow of reactant gases over the electrodes may be employed on the reactant gas side of the electrode. A one piece spacer may be used on the opposite side of the electrolyte plate to channel the products into a manifold for collection.

in a preferred arrangement, electrically conductive material is applied to the chamfered corners of the plates and spacers in a specified pattern. The conductive material pattern, when combined with a specified stacking pattern, facilitates the electrical interconnection of the plates electrically in series.

Preferably, the electrolyte elements are arranged into a stack so that alternate plates are arranged at 180° to each other. Electrode material on alternate successive elements, from one end of the stack to the other, may then be electrically connected in series by painting an electrically conductive material onto the chamfered corners of the plates. The electrical circuit is connected through the boltom plate in the stack, and may then proceed back up the stack in the opposite direction. 50 necting the electrodes previously bypassed.

Several advantages result from this electrical interconnection scheme. Every plate in the stack is an active ion conducting element. This aspect of the invention reduces the number of plates necessary for a given level of output resulting in increased efficiency of the device. Redundant electrical connection paths on more than one corner of the plates decreases the likelihood of elec-

trical circuit failure. Electrical resistance in the circuits between the electrolyte elements is also significantly reduced because the electrical paths are shorter are more efficient. Adjoining elements either receive reactant gases from a common reactant gas chamber, or dispense product gases into a common receiving chamber. This aspect of the invention enables electrical interconnection of the plates to be accomplished by painting an electrically conductive material onto the edges of the stack. Since the volume necessary for a given level of output by a given number of plates is significantly reduced, a stack of such plates contigured and structured in accordance with the invention reaches its operating temperature faster, and is more easily maintained at this temperature. This further contributes to the efficiency of the device.

Where all the structural components of the ion conducting device are constructed from the same ceramic material and are assembled and bonded into a stack, all the structural materials will necessarily have the same coefficient of thermal expansion. Cracks and distortions due to differing coefficients of thermal expansion are thus essentially eliminated.

The manufacturing method uses existing ceramic techniques allowing for inexpensive and rapid construction. Bonding the electrolyte elements into a stack and the application of electrodes and electrically conductive materials may be accomplished using well developed large scale manufacturing techniques. The method is thus suitable for large scale manufacture with existing technologies. The design and manufacturing method result in an ion conducting device which is efficient, reliable, and cost competitive.

The invention may be carried into practice in various ways and some embodiments will now be described by way of example with reference to the accompanying drawings, in which:

- Figure 1 is an exploded perspective view of an ion conducting device in accordance with the present invention:
- Figure 2 is an exploded perspective view of an ion conducting device of the instant invention illustrating the specified stacking pattern and the specified pattern of application of electrically conductive material to the chamfered corners of the electrolyte plates.
- Figure 3 is a side view of the device illustrating the flow chambers and the specified electrical interconnection scheme; and
- Figure 4 is a perspective view of an ion conducting device of the present invention illustrating the attachment of a product gas collecting manifold.
- Referring to Figure 1 and 2, an ion conducting device indicated generally as 10 includes a plurality of ion conducting electrolyte plates 14. The number of electrolyte plates employed depends on the desired capacity

of the device. The electrolyte plates 14 may be manufactured from any ion conducting material but are preferably from a ceramic metal oxide material. In one embodiment, the electrolyte material specifically conducts O^{-2} ions. Materials suitable for O^{-2} ion conduction include the metal oxides of cerium, zirconium, hafnium and bismuth. Electrolyte materials may be chosen in accordance with their ability to conduct the ions necessary for specific applications. In the arrangement shown in Figure 2, the electrolyte plates 14 have a pair of adjacent corners 16 and a pair of adjacent chamfered corners 18.

Electrode material 20 is attached to at least one flat surface of the electrolyte plates 14, but in the preferred embodiment illustrated, is attached to both sides of the plates. The electrode material 20 may be any gas permeable material which can be affixed to the electrolyte plates, and which can withstand the high (700-1000°C) operating temperature of the device. The electrode materials may be chosen based on their ability to conduct electrons, and their permeability or porosity to rapid flow of gas molecules. Materials particularly suitable for use as electrodes are noble metals such as silver and platnum, and ceramic materials such as lanthium-strontium-manganite. These materials have superior resistance to oxidation, and high conductivity at high temperature.

The electrode material 20 may be applied to the electrolyte plate by any suitable method, but in the preferred method, is applied by screenprinting. Screenprinting offers several advantages over other techniques. It is reproducible, inexpensive, and easy to perform. The electroded plate may then be thermally treated at a high temperature sufficient to bond the electrode 20 to the electrolyte 14 creating an electrolyte element. The temperature required for bonding varies for different electrode materials, but typically ranges from about 1000°C to 1400°C. A margin of unelectroded electrolyte surface 22 may be left at the edge of each electrolyte element.

An electrically conductive current collecting material (not shown) may be applied to the electrode surface 20 to distribute an electromotive force over the surface area of the electrode. The current collecting material is preferably a noble metal such as silver, a silver alloy, or platinum, and is applied to the electroded surface in a $^{-45}$ grid pattern. Since the current collector is less permeable to gas molecules the grid pattern distributes the electromotive force over the surface of the electrode, yet leaves the majority of electrode surface area available for the passage of gas molecules. The grid pattern also produces low sheet resistance to current passing through the current collector. In a preferred application method the current collector is screenprinted onto the electrode surface. Other methods such as painting may be used to apply the current collector to the electrode surface 20

In the arrangement shown in Figure 2, electrical interconnect stripes 36 are applied to the electrolyte

plates 14 to provide an electrical pathway between the electrode 20 and the square corners 16. The interconnect stripes 36 are an electrically conductive material which spans the unelectroded electrolyte margin 22. The electrical interconnect stripes 36 may be screen-printed onto the electrolyte plates, or applied by an alternative method such as painting.

A sealing material (not shown) such as glass may then be applied to the unelectroded margin 22 and allowed to dry. The sealing material may be applied by screenprinting, or by an alternative method such as painting. The sealing material must not melt or flow at the operating temperature of the stack.

The electrolyte elements may then be arranged into a stack as shown in Figures 1, 2 and 3, in which each element is separated from the element above and below by spacers. In the preferred arrangement illustrated, two types of spacers are alternately disposed between successive electrolyte element in the stack. The first spacer comprises a pair of spacer bars 24A and 24B. The spacer bars 24A and 24B may be positioned in the unelectroded margin 22, on opposite sides of the electrode material 20. When the spacer bars are sandwiched between a pair of electrolyte elements, a first chamber 26 having an inlet 28 and a first outlet 30. is defined, which is bounded by the spacer bars 24A and 24B, and the electrolyte elements above and below the spacer bars Reactant gases may flow through the first chamber 26, where they come in contact with the electrode surfaces The flow-through design facilitates a constant flow of fresh reactant gases through the first chamber 26.

The second spacer 32 is in the form of a U-shaped bar. The second spacer 32 is positioned in the unelectroded margin 22 on the opposite surface of the electrolyte elements from the first spacer. The orientation of second spacer 32 is such that the open end of the Ushape opens at 90° to the direction of flow through first chamber 26. When the second spacer 32 is sandwiched between a pair of electrolyte elements 14, a second chamber 34, having a second outlet 28 . is defined and bounded by the second spacer 32 and the electrolyte elements above and below. The second spacers 32 are all oriented in the stack so that the open ends of their respective U-shapes open at 90° to both the inlet 28 and the first outlet 30 of the first chamber 26. The single outlets 38 from the second chambers 34 allow a single manifold to be placed over all the respective outlets 38 to collect product gases from all of the second chambers

In the illustrated embodiment, the spacers 24A 24B and 32 are positioned on the unelectroded margin 22 to avoid obstruction of the ion conducting electrode surface, and to facilitate bonding of the spacers to the surface of the electrolyte elements. All corners of the first and second spacers are chamtered in this embodiment. The unelectroded margin 22 is disposed around the edge of the electrolyte plates because inadequate bonding would result if the spacers were placed on the electron.

trode

The spacers 24A, 24B and 32 are preferably manufactured from the same material as the electrolyte plates. Well known ceramic manufacturing methods, such as dry pressing, may be used to produce the spacers rapidly and inexpensively.

In the embodiments shown in Figure 2, each successive electrolyte element is oriented 180° from the corners 16 face in opposite directions on each successive element. The alternating pattern of assembly is thus as follows: an electrolyte element 14; a U-shaped second spacers 32, another electrolyte element 14 oriented 180° from the previous element; a pair of second spacer bars 24A and 24B oriented at 90° to the open end of the U-shaped second spacer 32 so that the inlet 28 and the first outlet 30 from the first chamber 26 are oriented at 90° to the second outlet 38; a third electrolyte element 14 oriented 180° from the previous element; another Ushaped second spacer 32 in the same orientation as the previous second spacer; another electrolyte element, 20 and so on in this pattern until the desired number of elements has been assembled into the stack.

The stack may then be thermally treated at a temperature sufficiently high to cause the sealing material to soften sufficiently that it bonds the electrolyte elements and spacers into a monolithic stack.

Referring to Figure 3, the stack of electrolyte elements and spacers may be connected in series electrically, to create a current based device. In the illustrated embodiment, when the electrolyte elements 14 and spacers 24A, 24B and 32 are assembled into a stack, the square corners 16 of the plates protrude out past the chamfered corners 18 of the plates above and below them, and the chamfered corners of the spacers. The electrical interconnect stripes 36 are located on the square corners 16 of the electrolyte elements 14, so they too protrude out past the chamfered corners of the spacers and plates. Because successive electrolyte plates are oriented 180° from the plates above and below, the electrical interconnect stripes 36 are exposed. That is to say, the interconnect stripes 36 are not sandwiched between the spacers, but protrude beyond the chamfered corners, and thus are accessible for electrical interconnection.

Series electrical connection of similarly oriented plates may be accomplished by applying an electrically conductive material, such as silver paint or paste, to the chamfered corners of the spacers 24A, 24B and 32, and to the chamfered corners of the electrolyte plates 14 above and below each similarly oriented plate. Other electrical interconnection schemes may be envisaged, such as attaching lead wires to notched spacers which are then sealed to the ends of the stack, to connect the electrolyte elements electrically according to the required electrical connection scheme.

This electrode electrical connection scheme is shown in Figures 2 and 3. An electrically conductive material 40 is in electrical contact with the interconnect

stripes 36 on the underside of the top electrolyte plate 14. The pathway of conductive material 40 thus goes from the interconnect stripe on one side of an electrolyte element, along the chamfered corner of the spacer below the plate, and the chamfered corner of the adverse oriented element, along the chamfered corner of the next spacer, to the top of the next protruding square corner which is an interconnect stripe of the next similarly oriented electrolyte element. The electrical interconnection then continues in this manner from the interconnect stripes on the bottom of this element. The similarly oriented elements are electrically connected in this manner, from one of the stack to the other. The plates having chamfered comers oriented at this corner of the stack are electrically bypassed because their interconnect stripes are 180° away on the opposite side of the stack.

The electrical pathway wraps around the bottom plate in the stack and proceeds up the opposite side of the stack. The plates having corners on the opposite side of the stack may be electrically connected in the same manner because their interconnect stripes are accessible on this side of the stack. Similarly, the plates previously electrically connected are bypassed because they have chamfered corners on this side of the stack. In following this pathway, the electrical connection pathway runs along the chamfered edge of a spacer, the electrically insulated chamfered corner of an electrolyte element, and another spacer's chamfered edge to the next stripe interconnect. This electrical connection scheme means that every alternate plate is electrically bypassed as the silver metallisation runs along the chamfered edges. The result is that a single stack is one series circuit and every whole plate in the stack is an active electrochemical cell.

Several significant advantages are afforded by this electrical interconnection scheme. Every plate in the stack is an active ion conducting element. The electrical interconnect scheme uses electrically conductive material applied to the exterior of the plates, so the need for electrically conductive interconnect plates is eliminated. This advantage also obviates the need to incorporate dissimilar materials into the stack having differing coefficients of thermal expansion. The redundant interconnect stripes and external electrical pathway also reduces the occurrence of open electrical circuits and leads to high reliability. If the external electrical pathway over requires attention, it is accessible and easily serviced.

Another advantage is that each of first chambers 26 is in fluid communication with two electrode surfaces on different plates. Ions are thus conducted from the reactant gases into a pair of plates instead of the usual one. Likewise, ion conduction products such as O₂, enter each second chamber 34 between two electrolyte elements. The stack is also better able to withstand stress by eliminating potentially weak points such as grooved interconnectors.

Referring to Figure 4, a manifold, indicated generally as 42, may be sealed to the stack. In the illustrated

embodiment, the manifold 42 includes a standoff 44 which spaces a manifold cover 46 away from the stack, and provides a seal against the stack. The standoff 44 and the manifold cover 46 may be hemetically sealed using glass frit to ensure a gas-tight seal. An outlet tube 45 is fixed to an aperture 50 in the manifold cover, to allow the product gases to be collected.

Claims

1. An electrochemical device (10) comprising a plurality of solid ion conducting electrolyte plates (14) and a plurality of spacers (24 32) disposed between successive electrolyte plates (14) with an individual 15 spacer (24) spacing adjacent electrolyte plates (14) apart, the electrolyte plates and spacer forming a monolithic stack, and in which the electrolyte plates (14) each have a pair of generally flat opposed surfaces with electrode material (20) adherent to a signiticant portion of each flat surface, the spaces between a plurality of successive pairs of spaced apart adjacent electrolyte plates (14) defining a plurality of chambers (26,34), the electrode material (20) on the flat electrolyte surfaces being electrically connected in series whereby the electrodes on alternate electrolyte plates (14) are electrically connected in series from one end of the stack to the other in a first electrical path, and the other alternate electrodes not connected in the first path are electrically connected in series in a second electrical path, the first and second path being connected together, the first and second paths and electrodes connected thereto thus forming a complete electrical circuit. characterised in that the spacers (24,32) include a 35 plurality of tirst spacers and plurality of second spacers, the first and second spacers alternating to separate successive electrolyte plates, each first spacer (24) consisting of a pair of bars and each second spacer (32) consisting of a U-shaped bar or multiple pieces configured and arranged to form a U-shaped bar the electrolyte plates (14) have at least one square corner (16) and at least one chamfered corner (18), the means for electrically connecting in series the electrode material on the electrolyte plates comprises at least one stripe (36) of electrically conductive material adherent to each of the first and second surfaces, the stripe (36) extending from the electrode material (20) to the edge of the square corner (16) thereby providing an electrical pathway between the electrode material (20) and the square corner (16); and the electrode material further comprises electrically conductive material adherent to the chamfered corners (18) of the electrolyte plates (14) and chamfered corners (18) 55 of the spacers (24,32) which thus form a plurality of electrical pathways

- A device as claimed in Claim 1, characterised in that
 the electrolyte plates (14) are formed from a metal
 oxide selected from zirconium oxide cerium oxide,
 hafnium oxide or bismuth oxide
- A device as claimed in Claim 1 or Claim 2, characterised in that the spacers (24.32) are constructed from the same material as the electrolyte plates (14), or from a material having a coefficient of thermal expansion which is substantially similar to that or the electrolyte plates (14).
- 4. A device as claimed in any preceding Claim, characterised in that a plurality of electrically conductive current collectors are attached to the electrode material (20), the current collectors being arranged to distribute an electromotive force over a significant portion of the electrodes
- A device as claimed in any preceding Claim, characterised by a manifold (42) attached to the device (10) for collecting products from ion conducting activity into a common outlet passage (48)
- 6. A device as claimed in any preceding Claim, characterised in that the electrolyte plates (14) have at least a first unelectroded margin (22) at the perimeter of the opposed surfaces.
- 30 **7**. A device as claimed in Claim 6, characterised in that the electrode plates have two neighbouring square comers (16), two chamfered corners, the electrolyte plates (14) are arranged in the stack so that each plate is orientated 180° from its adjacent plates, the first surfaces on successive plates are opposed, the second surfaces on successive plates are opposed. and the square corners (16) and the chamfered corners (18) on successive plates are located at mutually distinct edges of the stack, the first spacers (24) have chamfered corners and are sized to fit within the first unelectroded margin (22), the first spacers (24) being disposed between the opposed first surfaces of adjacent electrolyte plates (14) thereby defining a plurality of first chambers (26) between successive pairs of opposed first surfaces, the first chambers (26) having an inlet (28) and an outlet (30) for the flow of reactant gases therethrough, the second spacers (32) have chamfered corners and are sized to fit within the second unelectroded margin (22), the second spacers (32) being disposed between the opposed second surfaces of adjacent electrolyte plates (14) thereby defining a plurality of second chambers (34) having an outlet (35) or the evacuation of products each of the plurality of electrical pathways extending across a chamfered corner of one of the first spacers (24), a chamfered corner (18) of one of the electrolyte plates (14) and a chamfered corner of one of the second spacers

(32), these electrical pathways electrically connecting in series the stripes (36) on every alternate successive square corner (16).

- 8. A method of assembling and electrically connecting a plurality of solid oxide electrolyte plates (14) into a monolithic electrochemical ion conducting device (10) characterised by the steps of: applying electrode material (20) to a substantial portion of each of the two opposed surfaces of each of the electrolyte plates (14) heating the electroded electrolyte plates (14) to a temperature sufficient to bond the electrode material (20) to the electrolyte plates (14), applying an electrical interconnect material (36) to the electrolyte plates (14) to from an electrical pathway between the electrode materials (20) and the exterior of the device (10); applying sealing material to a portion of the electrolyte plates (14); stacking a plurality of the electrolyte plates (14) in a pattern in which each plate (14) is separated from adjacent 20 plates (14) by a solid oxide spacer (24,32); thermally treating a stack of the electrolyte plates (14) and spacers (24.32) at a temperature sufficient to activate the sealing material to seal the spacers (24.32) and the electrolyte plate (14) into a monolithic unit; electrically connecting in series every alternate electrolyte plate (14) in the stack by connecting the electrical interconnects (36) of every alternate plate (14) from one end of the stack to the other in a first electrical path, extending the electrical pathway around the end of the stack, and connecting the electrical interconnects (36) of every other alternate plate (14) in a second electrical pathway, the first and second electrical pathways and electrodes connected hereto forming a complete electrical circuit; and in which the spacers (24,32) include a plurality of first spacers and plurality of second spacers, the first and second spacers alternating to separate successive electrolyte plates, each first spacer (24) consisting of a pair of bars and each second spacer (32) consisting of a U-shaped bar or multiple pieces contigured and arranged to form a U-shaped bar; the electrolyte plates (14) have at least one square corner (16) and at least one chamfered corner (18); the means for electrically connecting in series the electrode material on the electrolyte plates comprises at least one stripe (36) of electrically conductive material adherent to each of the first and second surfaces, the stripe (36) extending from the electrode material (20) to the edge of the square corner (16) thereby providing an electrical pathway between the electrode material (20) and the square corner (16); and the electrode material further comprises electrically conductive material adherent to the chamfered corners (18) of the electrolyte plates (14) and chamfered corners (18) of the spacers (24,32) which thus form a plurality of electrical pathways.
- A method as claimed in Claim 8, characterised in that the electrode material (20) and/or the sealing material is applied by screen printing.
- 10. A method as claimed in Claim 9, characterised in that the electrode material (20) is applied to a central area of the electrolyte plates (14) and a margin (22) of the plate between the electrode material (20) and the edge of the plate (14) is left unelectroded.
 - A method as claimed in any of Claims 8 to 10. characterised in that the solid oxide spacers (24,32) are located in the margin (22) of unelectroded electrolyte surface.
 - 12. A method as claimed in any of Claims 8 to 11, characterised in that the electrical interconnect includes two stripes (36) of electrically conductive material screen printed onto the unelectroded margin (22) of electrolyte surface, the stripes (36) forming an electrical pathway between the electrode and the edge of the electrolyte plate (14).

Patentansprüche

 Elektrochemische Anordnung (10), die eine Viezahl Ionen-leitende Festelektrolytplatten (14) und eine Vielzahl Abstandshalter (24, 32) umfaßt, die zwischen aufeinanderfolgenden Elektrolytplatten (14) angeordnet sind, wobei mit einem einzelnen Abstandshalter (24) aneinandergrenzende, einzelne Elektrolytplatten (14) voneinander getrennt werden, wobei Elektrolytplatten und Abstandshalter einen monolithischen Stapel bilden, in welchem jede der Elektrolytplatten (14) ein Paar gewöhnlich flacher, einander entgegengesetzter Oberflächen mit Elektrodenmaterial (20) aufweist, das an einem signifikanten Teil einer jeden flachen Oberflache haftet, die Abstände zwischen einer Vielzahl aufeinanderfolgender Paare, von mit Zwischenräumen getrennt angeordneten, aneinandergrenzenden Elektrolytplatten (14) eine Vielzahl Kammern (26, 34) definieren, das Elektrodenmaterial (20) auf den flachen Elektrolytoberflächen elektrisch hintereinandergeschaltet ist, wobei die Elektroden auf altemierenden Elektrolytplatten (14) von einem Ende des Stapels zum anderen in einem ersten Strompfad elektrisch hintereinander verbunden sind, und die anderen, nicht in dem ersten Pfad verbundenen, alternierenden Elektroden elektrisch in einem zweiten Strompfad hintereinander verbunden sind, die ersten und die zweiten Pfade und Elektroden miteinander verbunden sind, und so einen vollständigen elektrischen Stromkreis bilden; dadurch gekennzeichnet daß die Abstandshalter (24, 32) eine Vielzahl erster Abstandshafter und eine Vielzahl zweiter Abstandshalter umfassen, wo-

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bei die ersten und die zweiten Abstandshalter alternierend die aufeinanderfolgenden Elektrolytplatten trennen, wobei jeder erste Abstandshalter (24) aus einem Paar von Stäben und jeder zweite Abstandshalter (32) aus einem U-förmigen Stab oder mehreren zu einem U-förmigen Stab zusammengestellten und angeordneten Stücken besteht, wobei die Elektrolytplatten (14) mindestens eine rechtwinklige Ecke (16) und mindestens eine abgeschragte Ecke (18) aufweisen wobei die Mittel, um das Elektrodenmaterial auf den Elektrolytplatten elektrisch hintereinander zu verbinden, mindestens einen Streifen (36) elektrisch leitenden Materials das an ieder der ersten und zweiten Oberflächen haftet. umfassen, wobei sich der Streifen (36), von dem 15 Elektrodenmaterial (20) zum Rand der rechtwinkligen Ecke (16) erstreckt und dadurch einen elektrischen Strompfad zwischen dem Elektrodenmaterial (20) und der rechtwinkligen Ecke (16) ermöglicht. und das Elektrodenmaterial (20) weiterhin elektrisch leitendes Material umfaßt, das an den abgeschrägten Ekken (18) der Elektrolytplatten (14) und der Abstandshalter (24, 32) haftet, die so eine Vielzahl Strompfade bilden.

- Anordnung nach Anspruch 1, gekennzeichnet durch Elektrolytplatten (14), die aus einen Metalloxid aus der Gruppe Zirconiumoxid, Ceroxid, Hafniumoxid oder Bismutoxid gebildet sind.
- Anordnung nach Anspruch 1 oder 2, gekennzeichnet durch Abstandshalter (24, 32), die aus dem gleichen Material wie die Elektrolytplatten (14) oder aus einem Material hergestellt worden sind, dessen thermischer Ausdehnungskoeffizient im wesentlichen dem der Elektrolytplatten (14) gleich ist
- 4. Anordnung nach einem der Ansprüche 1 bis 3 gekennzeichnet durch eine Mehrzahl von elektrischen leitenden Stromkollektoren, die an dem Elektrodenmaterial (20) befestigt sind, wobei die Stromkollektoren so angeordnet sind, daß sie eine elektromotorische Kraft über einen signifikanten Bereich der Elektroden verteilen.
- Anordnung nach einem der Ansprüche 1 bis 4 gekennzeichnet durch einen Verteiler (42), der an der Anordnung (10) befestigt ist, um die Produkte der Ionen-leitenden Aktivität in einen gemeinsamen Auslaß-Durchgangsweg (48) zu leiten
- Anordnung nach einem der Ansprüche 1 bis 5. gekennzeichnet durch Elektrolytplatten (14), die mindestens einen ersten von Elektroden freien Rand (22) am Umfang der entgegengesetzten Oberfläche aufweisen
- 7. Anordnung nach Anspruch 6. dadurch gekenn-

zeichnet, daß die Elektrodenplatten zwei benachbarte rechtwinklige Ecken (18) zwei abgeschragte Ecken aufweisen, wobei die Elektrolytplatten (14) in dem Stapel so angeordnet sind daß jede Platte unter 180° zu ihrer angrenzenden Platte orientiert ist, wobei die ersten Oberflächen auf aufeinanderfolgenden Platten entgegengesetzt sind, wobei die zweiten Oberflächen auf aufeinanderfolgenden Platten entgegengesetzt sind, und wobei die rechtwinkligen Ecken (16) und die abgeschragten Ecken (18) an aufeinanderfolgenden Platten wechselseitig an getrennten Kanten des Stapels angeordnet sind, wobei die ersten Abstandshalter (24) abgeschrägte Ecken haben und so bemessen sind, daß sie in den ersten Elektroden-freien Rand (22) passen, wobei die ersten Abstandshalter (24) zwischen den entgegengesetzten ersten Oberflächen der aneinandergrenzenden Eletrolytplatten (14) angeordnet sind, wodurch eine Mehrzahl von ersten Kammern (26) zwischen aufeinanderfolgenden Paaren von entgegengesetzten ersten Oberflächen detiniert werden, wobei die ersten Kammern (26) einen Einlaß (28) und einen Auslaß (30) für die hindurchströmenden Reaktionsgase aufweisen; wobei die zweiten Abstandshafter (32) abgeschrägte Ecken haben und so bemessen sind, daß sie in den zweiten Elektroden-freien Rand (22) passen: wobei die zweiten Abstandshalter (32) zwischen den entgegengesetzten zweiten Oberflächen der aneinandergrenzenden Elektrolytplatten (14) angeordnet sind, wodurch eine Mehrzahl von zweiten Kammern (34) definiert wird, die einen Auslaß (38) oder den Austrag der Produkte besitzt, wobei sich jeder der Mehrzahl der elektrischen Strompfade über eine abgeschrägte Ecke eines der ersten Abstandshalter (24) erstreckt, wobei eine abgeschrägte Ecke (18) von einer der Elektrolytplatten (14) und eine abgeschrägte Ecke von einem der zweiten Abstandshalter (32), diese Strompfade elektrisch in Serie der Bahnen (36) auf jeder aufeinanderfolgenden rechtwinkligen Ecke (16) verbindet.

Verfahren zum Zusammensetzen und elektrischen Verbinden einer Vielzahl von Festoxidelektrolytplatten (14) in einer monolithischen, elektrochemischen, lonenleitenden Anordnung (10), gekennzeichnet durch die Stufen. Aufbringen von Elektrodenmaterial (20) auf einen wesentlichen Teil jeder der beiden einander entgegengesetzten Oberflächen jeder der Elektrolytplatten (14) Erhitzen der mit Elektrodenmaterial versehenen Elektrolytplatten (14) auf eine ausreichend hohe Temperatur, um das Elektrodenmaterial (20) mit den Elektrolytplatten (14) zu verbinden. Aufbringen eines elektrischen Verbindungsmaterials (36) auf die Elektrolytplatten (14), um einen elektrischen Pfad zwischen den Elektrodenmaterialien (20) und der Außenseite der Anordnung zu bilden. Aufbringen eines Abdichtmaterials auf einen Teil der Elektrolytplatten (14); Stapeln einer Vielzahl von Elektrolytplatten (14) nach einem Muster, wobei jede Platte (14) von den aneinander angrenzenden Platten (14) durch einen Festoxidabstandshalter (24, 32) getrennt ist, thermische Behandlung eines Stapels von Elektrolytplatten (14) und Abstandshaltern (24, 32) bei einer Temperatur, die ausreichend ist, um das Abdichtmaterial für die Abdichtung der Abstandshalter (24, 32) und der Elektrolytplatten (14) unter Bildung einer monolithischen Einheit zu aktivieren;

elektrische Hintereinanderschaltung von allen alternierenden Elektrolytplatten (14) in dem Stapel, durch Verbinden der elektrischen Zwischenverbinder (36) jeder alternierender Platte (14) von einem Ende des Stapels bis zu dem anderen in einem ersten elektrischen Strompfad. Erstrecken des elektrischen Strompfads um das Stapelende und Verbinden der elektrischen Zwischenverbinder (36) jeder der anderen alterniereden Platten (14) in einem 20 zweiten Strompfad, der ersten und zweiten elektrischen Strompfade und der damit verbundenen Elektroden, die einen vollständigen elektrischen Stromkreis bilden; und wobei die Abstandshalter (24, 32) eine Vielzahl erster Abstandshalter und eine Vielzahl zweiter Abstandshalter umfassen, wobei die ersten und die zweiten Abstandshalter alternieren, um aufeinanderfolgende Elektrolytplatten zu trennen, wobei jeder erster Abstandshalter (24) aus einem Paar von Stäben und jeder zweite Ab-30 standshalter (32) aus einem U-förmigen Stab oder mehmen zu einem U-Stab geformten und angeordneten Stücken besteht, wobei die Elektrolyplatten (14) mindestens eine rechtwinklige Ecke (16) und mindestens eine abgeschrägte Ecke (18) aufweisen; wobei die Mittel, um das Elektrodenmaterial auf den Elektrolytplatten elektrisch hintereinander zu verbinden, mindestens einen Streifen (36) elektrisch leitenden Materials, das an jeder der ersten und zweiten Oberflächen haftet, umfassen, wobei sich der Streifen (36) von dem Elettrodenmaterial (20) zum Rand der rechtwinkligen Ecke (16) erstreckt und dadurch einen Strompfad zwischen dem Elektrodenmaterial (20) und der rechtwinkligen Ecke (16) ermöglicht; und wobei das Elektrodenmaterial (20) ferner elektrisch leitendes Material umfaßt, das an den abgeschrägten Ecken (18) der Elektrolytplatten (14) und der Abstandshalter (24, 32) haftet, die so eine Vielzahl elektrischer Strompfade bilden.

- Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das Elektrodenmaterial (20) und/oder das Abdichtmaterial mittels Siebdruck aufgebracht wird.
- Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das Elektrodenmaterial (20) auf einen zen-

- tralen Bereich der Elektrolytplatten (14) aufgebracht und ein Rand (22) der Platte zwischen dem Elektrodenmaterial (20) und der Kante der Platte (14) frei vom Elektrodenmaterial belassen wird.
- Verfahren nach einem der Ansprüche 8 bis 10, dadurch gekennzeichnet, daß die Festoxidabstandshalter (24, 32) in dem Rand (22) der von Elektroden freien Elektrolytoberfläche angeordnet sind.
- 12. Verfahren nach einem der Ansprüche 8 bis 11, dadurch gekennzeichnet, daß die elektrischen Zwischenverbindungen zwei Streifen (36) elektrisch leitendes Material umfassen, das durch Siebdruck auf den Elektroden-freien Rand (22) der Elektrolytoberfläche aufgebracht wird und die Streifen (36) zwischen der Elektrode und der Kante der Elektrolytplatte (14) einen Strompfad bilden.

Revendications

- Dispositif électrochimique (10) comprenant un certain nombre de plaques d'électrolyte solide conductrices d'ions (14) et un certain nombre d'entretoises (24, 32) disposées entre plaques d'électrolyte (14) successives, de laçon qu'une entretoise individuelle (24) espace l'une de l'autre des plaques d'électrolyte (14) adjacentes, les plaques d'électrolyte et les entretoises formant une pile monolithique, et dans lequel : les plaques d'électrolyte (14) comportent chacune une paire de surfaces opposées généralement plates avec un matériau d'électrode (20) adhérent à une partie importante de chaque surface plate; les espaces entre un certain nombre de paires successives de plaques d'électrolyte adjacentes espacées (14), définissant un certain nombre de chambres (26, 34), le matériau d'électrode (20) se trouvant sur les surfaces d'électrolyte plates étant connecté électriquement en série de façon que les électrodes sur des plaques d'électrolyte alternées (14) soient branchées électriquement en série d'une extrémité de la pile à l'autre dans un premier chemin de conduction électrique, et que les autres électrodes alternées, non branchées dans le premier chemin, soient branchées électriquement en série dans un second chemin de conduction électrique, le premier chemin et le second chemin étant connectés l'un à l'autre, ce premier chemin, ce second chemin et les électrodes branchées à ceux-ci, formant ainsi un circuit électrique complet ; 50 caractérisé en ce que
 - les entretoises (24, 32) comprennent un certain nombre de premières entretoises et un certain nombre de secondes entretoises, les premières et les secondes entretoises étant alternées pour séparer des plaques d'électrolyte successives, chaque première entretoise (24) étant constituée d'une paire

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de barres et chaque seconde entretoise (32) étant constituée d'une barre en forme de U ou de pièces multiples configurées et disposées pour former une barre en forme de U les plaques d'électrolyte (14) comportent au moins un coin carré (16) et au moins un coin chanfreiné (18) les moyens pour connecter électriquement en série le matériau d'électrode sur les plaques d'électrolyte, comprennent au moins une bande (36) de matériau électriquement conducteur adhérent à chacune des première et seconde surfaces, la bande (36) allant du matériau d'électrode (20) jusqu'au bord du coin carré (16) pour fournir ainsi un chemin de conduction électrique entre le matériau d'électrode (20) et le coin carré (16) et le matériau d'électrode comprend en outre un 15 matériau électriquement conducteur adhérent aux coins chanfreinés (18) des plaques d'électrolyte (14) et aux coins chanfreinés (18) des entretoises (24, 32) pour former ainsi un certain nombre de chemins de conduction électrique.

2. Dispositif selon la revendication 1. caractérisé en ce que les plaques d'électrolyte (14) sont réalisées en un oxyde métallique choisi parmi l'oxyde de zirconium. l'oxyde de cérium. l'oxyde de hafnium ou l'oxyde de bismuth

3. Dispositif selon la revendication 1 ou la revendication 2. caractérisé en ce que les entretoises (24 32) sont réalisées à partir du même matériau que les plaques d'électrolyte (14), ou à partir d'un matériau ayant un coefficient de dilatation thermique qui soit essentiellement analo- 35 gue à celui des plaques d'électrolyte (14)

4. Dispositif selon l'une quelconque des revendications précédentes caractérisé en ce qu' un certain nombre de collecteurs de courant électriquement conducteurs sont fixés sur le matériau d'électrode (20), ces collecteurs de courant étant disposés pour répartir une force électromotrice sur une partie importante des électrodes

5. Dispositif selon l'une quelconque des revendications précédentes caractérisé par une tubulure (42) fixée au dispositif (10) pour collecter, dans un passage de sortie commun (48). les produits provenant de l'activité de conduction d'ions

Dispositif selon l'une quelconque des revendica- 55 tions précédentes caractérisé en ce que les plaques d'électrolyte (14) comportent au moins

une première marge (22) non transformée en électrode à l'endroit du périmètre des surfaces opposées

Dispositif selon la revendication 6. caractérisé en ce que les plaques d'électrode comportent deux coins carrés voisins (16) et deux coins chanfreinés, les plaques d'électrolyte (14) sont disposées dans la pile de façon que chaque plaque soit orientée à 180° de ses plaques adjacentes, les premières surfaces sur des plaques successives sont opposées, les secondes surfaces sur des plaques successives sont opposées et les coins carrés (16) ainsi que les coins chanfreinés (18) sur des plaques successives, sont placés à l'endroit de bords mutuellement distincts de la pile. les premières entretoises (24) comportent des coins chanfreines et sont dimensionnées pour s'adapter à l'intérieur de la première marge non transformée en électrode (22). les premières entretoises (24) étant disposées entre les premières surfaces opposées de plaques d'électrolyte adjacentes (14) pour définir ainsi un certain nombre de premières chambres (26) entre les paires successives de premières surfaces opposées. les premières chambres (26) ayant une entrée (28) et une sortie (30) pour l'écoulement des gaz de réaction à travers celles-ci : les secondes entretoises (32) comportent des coins chanfreinés et sont dimensionnées pour s'adapter à l'intérieur de la seconde marge (22) non transformée en électrode. les secondes entretoises (32) étant disposées entre les secondes surfaces opposées de plaques d'électrolyte (14) adjacentes pour définir ainsi un certain nombre de secondes chambres (34) ayant une sortie (38) pour l'évacuation des produits chacun de la pluralité des chemins de conduction électrique passant par un coin chanfreiné de l'une des premières entretoises (24), un coin chanfreiné (18) de l'une des plaques d'électrolyte (14), et un coin chanfreiné de l'une des secondes entretoises (32), ces che-

Procédé pour assembler et connecter électriquement un certain nombre de plaques d'électrolyte à oxyde solide (14) de manière à former un dispositif conducteur d'ions électrochimique monolithique (10)

mins de conduction électrique branchant électri-

quement en série les bandes (36) sur chaque coin

caractérisé par les étapes consistant à

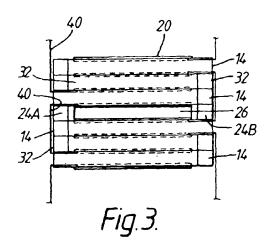
carré alterné successif (16)

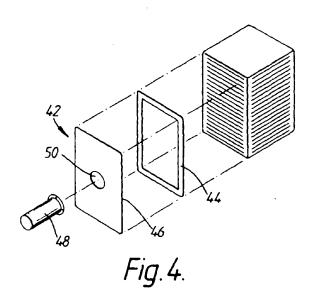
appliquer un matériau d'électrode (20) à une partie importante de chacune des deux surfaces opposées de chacune des plaques d'électrolyte (14), en chauffant les plaques d'électrolyte (14) transformées en électrodes, jusqu'à une température suffisante pour coller le matériau d'electrode (20) aux plaques d'électrolyte (14)

- appliquer un matériau d'interconnexion électrique (36) aux plaques d'électrolyte (14) de manière à former un chemin de conduction électrique entre les matériaux d'électrode (20) et l'extérieur du dispositif (10);
- appliquer un matériau d'étanchéité à une partie des plaques d'électrolyte (14)
- empiler un certain nombre des plaques d'électrolyte (14) suivant une configuration dans laquelle chaque plaque (14) est séparée des plaques (14) adjacentes par une entretoise en oxyde solide (24, 32);
- traiter thermiquement une pile des plaques d'électrolyte (14) et des entretoises (24. 32) à une température suffisante pour activer le matériau d'étanchéité de manière à sceller les entretoises (24, 32) à la plaque d'électrolyte (14) pour former un bloc monolithique
- brancher électriquement en série chaque plaque d'électrolyte alternée (14) de la pile en connectant les interconnexions électriques (36) de chaque plaque alternée (14) d'une extrémité à l'autre de la pile dans un premier chemin de 25 conduction électrique, en prolongeant le chemin de conduction électrique autour de l'extrémite de la pile et en connectant les interconnexions électriques (36) de chaque autre plaque alternée (14) dans un second chemin de conduction électrique, le premier chemin et le second chemin de conduction électrique ainsi que les électrodes connectées à ceux-ci, formant un circuit électrique complet
- et dans lequel les entretoises (24, 32) comprennent un certain nombre de premières entretoises et un certain nombre de secondes entretoises, les premières et les secondes entretoises étant alternées pour séparer des plaques d'electrolyte successives, chaque première entretoise (24) étant constituée d'une paire de barres, et chaque seconde entretoise (32) étant constituée d'une barre en forme de U ou de pièces multiples configurées et disposées pour former une barre en forme de U : les plaques d'électrolyte (14) comportent au moins un coin carré (16) et au moins un coin chanfreiné (18) : les moyens pour brancher électriquement en série le matériau d'électrode sur les plaques d'électrolyte, comprenant au moins une bande (36) de matériau électriquement conducteur adhérent à chacune des première et seconde surfaces, la bande (36) s'étendant du matériau d'électrode (20) jusqu'au bord du coin carré (16) pour fournir ainsi un chemin de conduction 55 électrique entre le matériau d'électrode (20) et le coin carré (16); et le matériau d'électrode comprenant en outre un matériau électrique-

ment conducteur adhérent aux coins chanfreinés (18) des plaques d'électrolyte (14) et aux coins chanfreines (18) des entretoises (24, 32), pour former ainsi un certain nombre de chemins de conduction électrique.

- 9. Procédé selon la revendication 8, caractérisé en ce que
 - le matériau d'électrode (20) et/ou le matériau d'étanchéité est appliqué par impression à l'écran (sérigraphie).
- Procédé selon la revendication 9.
 - caractérisé en ce que le matériau d'électrode (20) est appliqué à une zone centrale des plaques d'électrolyte (14) et une marge (22) de la plaque entre le matériau d'électrode (20) et le bord de la plaque (14), est laissée sans être transformée en électrode.
- 11. Procédé selon l'une quelconque des revendications
 - caractérisé en ce que
 - les entretoises d'oxyde solide (24, 32) sont placées dans la marge (22) de la surface d'électrolyte non transformée en électrode.
- 12. Procédé selon l'une quelconque des revendications 8 à 11,
 - caractérisé en ce que
 - l'interconnexion électrique comprend deux bandes (36) d'un matériau électriquement conducteur imprime à l'écran sur la marge (22) non transformée en électrode, de la surface de l'électrolyte, les bandes (36) formant un chemin de conduction électrique entre l'électrode et le bord de la plaque d'électrolyte (14).





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24B

-14 22

-36 -20

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